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The Absorption Spectrum of the Anthracene Molecule in the Vacuum Ultraviolet

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The Absorption Spectrum of the Anthracene Molecule in the Vacuum Ultraviolet[+]

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The optical absorption of anthracene vapour for photon energies from 5 to 8.5 eV was found to differ substantially from the spectra reported earlier for parts of this range[1,2]*. Above the strong* $^1B_{2u}$ *long axis polarized* $\pi-\pi^*$ *transition at 5.24 eV three short axis polarized* $^1B_{1u}$ $\pi-\pi^*$ *transitions are assigned on the basis of the oriented gas model in comparison to spectra from anthracene single crystals. A tentative new assignment for most of the additionally observed sharp Rydberg bands leading to the first ionization potential at 7.47 eV is given.*

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In organic solid state physics anthracene serves as a standard substance for both the investigation of semiconducting properties and for the study of molecular excitons[3]. Although the electronic properties of the solid are closely related to those of the molecule up to now only little is known about the electronic transitions of the molecule in the ultraviolet not influenced by solvent effects.

Here we would like to give our first results of an investigation of the absorption spectrum of the molecule in the range 5 to 8.5 eV (2500 Å to 1460 Å). Parts of this spectral range have already been studied by Lyons and Morris[1] and by Angus and Morris[2]. These investigations gave contradictory results for the spectral range common to both. The absorption spectrum of anthracene in n-heptane solution has been measured by Klevens and Platt for photon energies up to 7 eV[4]. From these measurements it is difficult to deduce transition energies with sufficient accuracy since considerable shifts due to the solvent have to be expected. In the past some information about the transition energies for the free molecule could be obtained from studies of electron energy loss spectra[5,6]. These experiments, however, were limited by the comparatively low resolution of 0.5 eV. The aim of our present study was to get more detailed information about the molecular transitions and to compare it with ε-spectra from anthracene single crystals[7].

Experimental details were given in previous publications[8,9]. The synchrotron radiation from DESY was used as a continuous light source. Spectra were recorded photographically with a 2.2 m grazing incidence spectrograph. In addition they were measured photoelectrically using a vertical normal incidence Wadsworth monochromator. The wavelength resolution was approximately

1 Å (corresponding to 10 meV at 10 eV). The photon energies given with our results are correct within ±0.015 eV. Polycrystalline anthracene from Rüttgerswerke AG with a purity of 99.9 % was used as sample material without further purification. It was kept at 80° C in the absorption cell with LiF-windows for several hours in order to outgas the material. The spectra were recorded at 92° C at a vapour pressure of about 0.013 Torr.

The absorption spectrum thus obtained between 5 and 8.5 eV is shown in Fig. 1. Our results differ quite markedly from the spectra reported earlier for parts of this range[1,2]. On the other hand, they are in excellent agreement with data obtained by Clark[10].

A strong absorption band is observed with its maximum at 5.24 eV (Fig. 1) as well as additional diffuse vibrational structures seen as shoulders at 5.28, 5.40, and 5.56 eV. This band has already been observed in photoabsorption measurements[1] as well as in electron energy loss spectra[5,6]. In spectra taken in n-heptane solution it is redshifted to 4.84 eV[4]. In agreement with theoretical calculations[11] this intense band has been interpreted as a long axis (L) polarized π-π^* transition of symmetry type ${}^1B_{2u} \leftarrow {}^1A_{1g}$. (The notation follows the convention as given in J.Chem.Phys. 23, 1197 (1955)). A clear proof for this assignment is given by the analysis within the oriented gas model of our reflection and derived ε_2- spectra obtained for anthracene single crystals for photon energies from 4.5 to 11.5 eV[7]. As long as the intensity ratios, as given by the oriented gas model, are not reversed by the crystal interaction, three ${}^1B_{1u}$-transitions of medium intensity polarized along the short molecular axis (M) are expected according to the crystal spectra at higher energies between 5 and 9 eV. The observed absorption bands with their centers at about 5.8 eV (shoulder), 6.9 and 8.1 eV (Fig. 1) may be assigned to these $^1B_{1u}$ π-π^* transitions. The magnitude of the observed crystal shift of these bands of the order of 0.5 eV (table 1) is quite plausible in view of the large redshift from 5.24 eV to 4.56 eV for the strong L-polarized $^1B_{2u}$ transition. Our results and assignments for the most prominent π-π^* N-V transitions are summarized in table 1. Comparison of the vapour and solution data clearly shows the need to compare vapour-data to calculated transition energies since solvent effects cannot be neglected. The calculation of these shifts is as yet impractical[12].

The sharp maxima at 6.26, 6.43 and 6.53 eV and the bands superimposed on the 6.9 eV M-band belong to Rydberg series. Angus and Morris assigned 5 series[2]. From these they deduced a value of 7.15 eV for the first ionization potential. We are unable to confirm this assignment on the basis of our spectra. Recent photoelectron spectra show the first four ionization potentials due to the removal of the outer π-electrons to fall at 7.47 eV ($2b_{2g}$), 8.57 eV ($2b_{1g}$), 9.23 eV ($1a_u$) and 10.26 eV ($2b_{3u}$)[13]. (We have changed the notation of Ref. 13 according to the convention for the notation mentioned above.) As for benzene[8] and naphthalene[9] the presence of Rydberg series to higher ionization potentials as well as the occurence of additional vibrational bands makes an unequivocal assignment difficult. In Fig. 1 we have tentatively indicated two series with quantum defects $\delta=0.64$ and $\delta=0.2$ which account for several of the most prominent bands. They both lead to the first ionization potential at 7.47 eV and are accompanied by vibrational bands with a dominating vibrational energy of 0.16 to 0.17 eV. This vibrational energy, also observed for the $^1B_{2u}$ N-V absorption band at 5.24 eV, is associated with a totally symmetric normal mode of the carbon skeleton[14]. The good correspondence of the vibrational structure between these Rydberg bands and the photoelectron spectrum for the first ionization potential[13] confirms our assignment. According to the selection rules and the magnitude of the quantum defect the series with $\delta=0.64$ is an allowed p-type Rydberg series $2b_{2g}\rightarrow npb_{1u}$, the transitions being polarized perpendicular to the molecular plane. The series with $\delta=0.2$ is probably the second allowed p-type series $2b_{2g}\rightarrow npb_{3u}$, with transitions polarized along the short molecular axis.

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Table 1

Position (in eV) and assignment for the most prominent π-π^{*} transitions of anthracene. B_{1u} and B_{2u} correspond to short and long axis polarization respectively. The labeling of transitions by Klevens and Platt is given for comparison. For solid anthracene maxima in ε_2 are denoted together with the particular polarization direction (see ref. d) and the limits in accuracy introduced by the Kramers Kronig analysis.

vapour[a]		solution in n-heptane[c]		solid[d]	
3.45[b]	$^1B_{1u}$	3.27	^1La	3.13±0.03[e]	E ∥ b on (001)
5.24	$^1B_{2u}$	4.84	^1B_b	4.56±0.03	E ∥ L on (010)
~5.8 sh	$^1B_{1u}$	5.62	^1C_b	5.56±0.05	E ∥ M on (010)
~6.9	$^1B_{1u}$	6.66	^1B_a	6.30±0.1	E ∥ M on (010)
~8.1	$^1B_{1u}$			7.5 ±0.1	E ∥ M on (010)

sh: shoulder

a this work

b E.E. Koch, S. Kunstreich, and A. Otto, Opt.Commun. 2, 365 (1971)

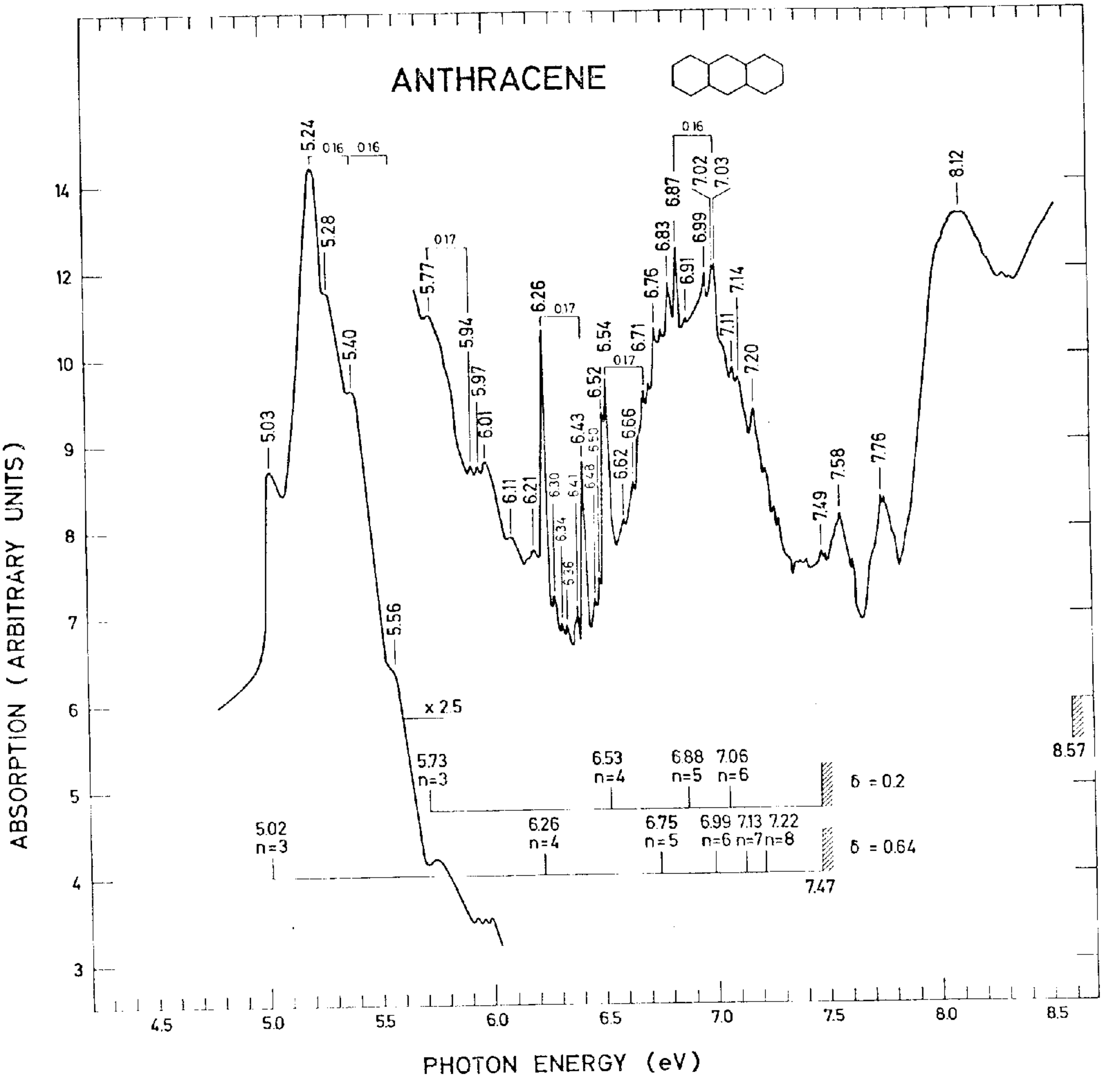
c H.B. Klevens and J.R. Platt, J.Chem.Phys. 17, 470 (1949)

d E.E. Koch and A. Otto, phys.stat.sol. (b) 51, 69 (1972)

e L.B. Clark and M.R. Philpott, J.Chem.Phys. 53, 3790 (1970)

Figure captions

Fig. 1: Densitometer trace of the absorption spectrum of anthracene vapour from 5 to 8.5 eV. The incoming intensity is nearly constant over this range. Indicated Rydberg series have been calculated with the given quantum defects, values for the ionization potentials are taken from Ref. 13.


ANTHRACENE
ABSORPTION (ARBITRARY UNITS)
PHOTON ENERGY (eV)
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
3
4
5
6
7
8
9
10
12
14
5.03
5.24
0.16
0.16
5.28
5.40
5.56
x 2.5
5.77
0.17
5.94
5.97
6.01
6.11
6.21
6.26
0.17
6.30
6.34
6.36
6.41
6.43
6.48
6.50
6.52
6.54
0.17
6.62
6.66
6.71
6.76
6.83
6.87
0.16
6.91
6.99
7.02
7.03
7.11
7.14
7.20
7.49
7.58
7.76
8.12
8.57
5.73
n=3
6.53
n=4
6.88
n=5
7.06
n=6
δ = 0.2
5.02
n=3
6.26
n=4
6.75
n=5
6.99
n=6
7.13
n=7
7.22
n=8
δ = 0.64
7.47